

## PATENT SPECIFICATION

NO DRAWINGS

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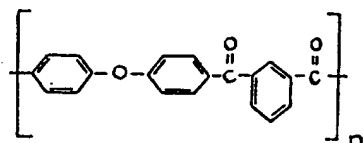
## COMPLETE SPECIFICATION

## Polymeric Ketones

- 5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

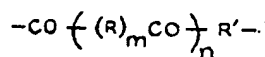
- 10 This invention relates to fibre and film forming polyketones.

It is known to prepare a low molecular weight aromatic polyketone of the following formula:



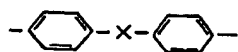
- 15 (See the paper by R. H. Michel and W. A. Murphey, Journal of Polymer Science, 1961, 55, pages 741 to 751).

- 20 According to the present invention we provide fibre and film forming, high molecular weight polyketones, as hereinafter defined, containing the repeating unit:

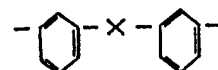


where R is a radical chosen from the group consisting of

- 25 (i) a divalent aliphatic radical,  
(ii) a divalent radical chosen from the group consisting of



and



30

where X is chosen from the group consisting of —CO— and —SO<sub>2</sub>— and each aromatic nucleus may be unsubstituted, as shown, or may contain from one to four substituents each of which may be chosen from the group consisting of CH<sub>3</sub>—, CH<sub>3</sub>O—, C<sub>2</sub>H<sub>5</sub>O—, C<sub>2</sub>H<sub>5</sub>O—, F—, Cl— and Br—,

35

(iii) a divalent aromatic radical which may be mono or bi nuclear and may be a condensed ring nucleus and the nucleus in each case may be unsubstituted or may be substituted in the manner described in (ii).

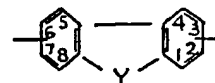
40

(iv) a mixed alkyl/aryl diradical, the aromatic nucleus of which may be unsubstituted or may be substituted in the manner described in (ii).

45

R<sup>1</sup> is a radical chosen from the group consisting of

(a)

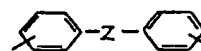


where Y is —O—, —CH<sub>2</sub>— or —S— which may be unsubstituted, as shown, or may be substituted in either or both aromatic nuclei by from one to three substituents each of which may be chosen from the group consisting of alkyl, alkoxy, F—, Cl and Br—

50

55

(b)



where Z is —A—, —O—A—O—, —S—, —CH=CH—, —CH<sub>2</sub>—O—CH<sub>2</sub>—, —O— or a direct linkage

5 A is alkylene

and either or both of the aromatic nuclei may be unsubstituted or may be substituted with one to four substituents each of which may be chosen from the group consisting of

10 alkyl, alkoxy, F—, Cl— and Br—.

m is zero or one

n is zero or one.

By the term polymeric ketones we mean products containing the above repeating units and also those polymeric ketones wherein a proportion of the units are replaced by other units, such for example, as units similar to those shown above wherein R, R<sup>1</sup>, m and n may each have a significance different from that in the units of which the major part of the molecule is constructed.

The polymeric ketones of our invention can be prepared by a variety of methods among which are the following:

25 1. The reaction of the compound H—R<sup>1</sup>—H with an acid chloride.

This reaction may be carried out under the influence of a Friedel - Crafts catalyst, such as aluminium trichloride; aluminium tri-  
30 bromide; boron trifluoride; hydrofluoric acid; ferric chloride; stannic chloride; titanium tetrachloride; phosphoric acid; phosphorus pentoxide or mixtures of phosphoric acid and phosphorus; pentoxide; hydrochloric acid; sulphuric acid and arylsulphonic acids.

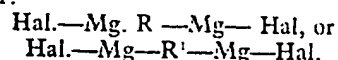
35 Examples of compounds of the formula H—R<sup>1</sup>—H are: fluorene; bibenzyl; 1:3 - diphenyl - propane; 2:2 - diphenylpropane; 1:4 - diphenyl - butane; 1:10 - diphenyl -  
40 decane; 1:2 - diphenoxyethane; 1:3 - diphenoxypropane; 1:4 - diphenoxybutane; 1:3 - diphenoxy - 2:2 - dimethylpropane; 1:10 - diphenoxydecane; stilbene; dibenzyl ether; 2 - methylbiphenyl; 2:2<sup>1</sup> - dimethyl-  
45 biphenyl; 3 - methylbiphenyl; 2 - chlorobiphenyl; 2 - methyldiphenyl ether; 2:2<sup>1</sup> - dimethyldiphenyl ether; 3 - methyldiphenyl ether; 2:2<sup>1</sup> - dichlorodiphenyl ether; 2:2<sup>1</sup> -  
50 dimethyl - 6:6<sup>1</sup> - dichlorodiphenyl ether; 2 - chlorodiphenyl ether; 2 - fluorobiphenyl; 3 - fluorobiphenyl; 2:2<sup>1</sup> - dimethoxybiphenyl; 2 - methyl - 2<sup>1</sup> - methoxybiphenyl; 2:4:2<sup>1</sup>:4<sup>1</sup> - tetramethyldiphenyl ether; 3:5:3<sup>1</sup>:5<sup>1</sup> - tetra-  
55 methyldiphenyl ether; 1:2 - di - (2 - methylphenoxy) ethane; 2:2<sup>1</sup> - dimethyl - diphenylmethane; 2:2<sup>1</sup> - dimethyldibenzyl ether; 2 - methoxystilbene; 4:5 - dimethylfluorene; 1:8 - dimethoxyfluorene; 4 - chlorodibenzofuran.

60 Suitable di - acid chlorides for this reaction include the following: isophthaloyl chloride; terephthaloyl chloride; methoxyterephthaloyl chloride; ethoxyterephthaloyl chloride; propoxyterephthaloyl chloride; isopropoxyterephthaloyl chloride; fluoroterephthaloyl chlo-

ride; chloroterephthaloyl chloride; methylterephthaloyl chloride; methylisophthaloyl chloride; chloroisophthaloyl chloride; alkoxyisophthaloyl chloride; the diacid chloride of 4:4<sup>1</sup> - dicarboxydiphenylmethane; the diacid  
70 chloride of 3:3<sup>1</sup> - dicarboxydiphenylmethane; bibenzyl - 4:4<sup>1</sup> - dicarbonyl chloride; phosgene; oxalyl chloride; adipoyl chloride; sebacoyl chloride; glutaryl chloride; 3 - oxaglutaryl chloride; 2 and 3 alkyl substituted glutaryl chloride; pimeloyl chloride; suberoyl  
75 chloride; azelaoyl chloride; mono- and disubstituted malonyl chloride; fumaroyl chloride; dichloroterephthaloyl chloride; dichloroisophthaloyl chloride; dimethylterephthaloyl chloride; dimethylisophthaloyl chloride; diphenyl ether dicarbonyl chlorides, naphthalene-  
80 1:4-; -1:5-; -2:6- and -2:7 - dicarbonyl chlorides; homoterephthaloyl chloride; homoisophthaloyl chloride; meta- and para - phenylenediacetyl chlorides; cyclopentane-1:3-dicarbonyl chloride; cyclohexane - 1:3- and 1:4 - dicarbonyl chlorides; furan - 2:5 - dicarbonyl chloride and tetra - hydrofuran -  
85 2:5 - dicarbonyl chloride. The Friedel - Crafts reaction is conveniently carried out in the presence of a suitable solvent, such for example as a chlorinated hydrocarbon, nitrobenzene or carbon bisulphide. The Friedel - Crafts reaction may, in favourable cases, as demonstrated by Nenitzescu et al (Anm., 1931, 491, 210), be carried out in the absence of catalyst.

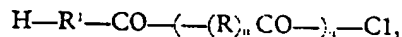
2. The reaction of the compound H—R<sup>1</sup>—H with a di-acid or its anhydride.

3. The reaction of Grignard reagents of the  
90 formula:

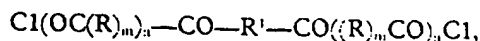


where Hal represents halogen, with a dinitrile of appropriate formula, followed by hydrolysis.  
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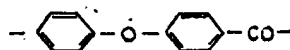
4. A Friedel-Crafts reaction between compounds which may be regarded as intermediates in methods (1) and (2) above, although they may be prepared by other known methods. Thus self-condensation of compounds of the  
110 structure:



or otherwise by condensation of compounds of the structure HR<sup>1</sup>H with compounds of the structure  
115



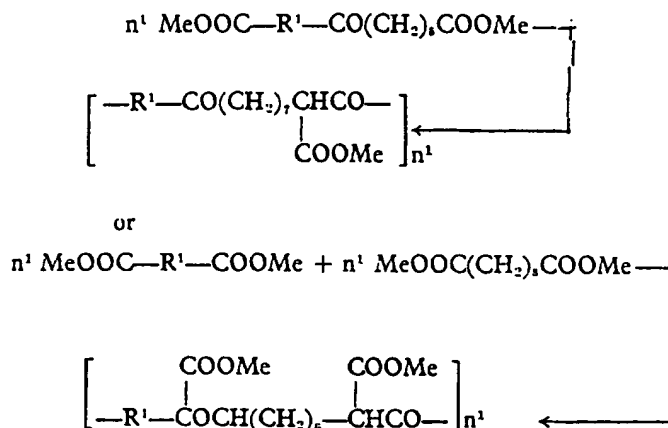
where R, R<sup>1</sup>, m and n are as defined above, may be employed to give the products of this invention. For example, the polyketone containing the repeat unit:  
120



may be prepared by reaction of diphenyl ether with phosgene, by the polycondensation of diphenyl ether - 4 - carbonyl chloride or by the

reaction of diphenyl ether with diphenyl ether-4:4'-dicarbonyl chloride.

5. A Claisen condensation of one of the types:



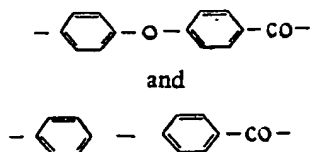
where  $n^1$  is an integer, followed in either case by hydrolysis to the resulting keto-acid, which readily decarboxylates to the ketone. This method is not available for the preparation of polymers where  $m$  or  $n$  is zero.

15 polymers where m or n is zero.

The copolymers which also form part of our invention are prepared by similar methods but using mixtures of the appropriate acids, acid derivatives, Grignard reagents or other

20 reactable materials. Thus a copolymer containing the units

The copolymers which also form part of our invention are prepared by similar methods but using mixtures of the appropriate acids, acid derivatives, Grignard reagents or other reactable materials. Thus a copolymer containing the units



25 may be prepared by, for example, the reaction of a mixture of biphenyl and diphenyl ether, in the desired proportions, with phosgene.

The following examples, in which all parts are by weight, illustrate, but do not limit, the scope of our invention.

### EXAMPLE 1

*Poly(sebacoyldiphenyl ether)*

Diphenyl ether (4.35 parts) was dissolved in dry methylene chloride (50 parts) and the mixture was cooled to  $-65^{\circ}\text{C}$ . Aluminium chloride (9.35 parts) was added followed after 5 minutes vigorous stirring by sebacyl chloride (6.0 parts). The temperature rose to  $-50^{\circ}\text{C}$ . then returned to  $-65^{\circ}\text{C}$ ; the mixture was allowed to warm during 3 hours to room temperature, then refluxed on a steam-bath for  $\frac{1}{2}$  hour. The product was decanted into dilute hydrochloric acid (100 parts), and this mixture was heated on a steam-bath for  $\frac{1}{2}$  hour and then filtered. In addition to the polymeric product so isolated, some was found to be present in the reaction flask in the form of a

film on the walls which was not only coherent but very tough. The polymer was purified by precipitation from a solution in orthochlorophenol by light petroleum. The product had a Viscosity Ratio (measured on a 1% solution in ortho-chlorophenol at 25°C) of 3.58, and a crystalline melting point of 195°C.

The poly(4:4'-sebacoyl diphenyl ether) (2 parts) was dissolved in ortho-chlorophenol (20 parts) to give a viscous homogeneous solution which was extruded from a hypodermic syringe through a size 'O' needle into a coagulating bath of methanol at room temperature. The fibre formed by drawing the extruded polymer away from the needle was allowed to dry in air then hand-drawn on a metal surface at 140–160°C. A draw ratio of approximately 5:1 was obtained. The resulting fibres had an average denier of 51, an average tenacity of 2.5 g.p.d., and an average extensibility of 23%. The X-ray diffraction pattern of the drawn fibres showed them to be highly crystalline and slightly oriented.

Acetone and ethyl acetate were also found to be suitable for use in coagulating baths for forming the fibres.

### EXAMPLE 2

*Poly(adipolydihenyl ether)*

Diphenyl ether (4.25 parts), dry methylene chloride (25 parts), aluminium chloride (9.35 parts), and adipoyl chloride (4.6 parts) were reacted as in Example 1. The polymer obtained, without purification by precipitation from ortho-chlorophenol, had a Viscosity Ratio (measured on a 1% solution in ortho-chlorophenol at 25°C) of 1.44, and a crystalline melting point of 240°C.

### EXAMPLES 3—5

The following polymers were prepared as described in Example 1, but using the acid chlorides listed instead of sebacoyl chloride:

Ex.	Acid Chloride (parts)	Polymer	Birefringent melting point	Viscosity Ratio
3	Azelaoyl (5.63)	Poly(azelaoyl-diphenyl ether)	188—192°C.	1.38
4	Suberoyl (5.28)	Poly(suberoyl-diphenyl ether)	210—220°C.	2.86
5	Pimeloyl (4.93)	Poly(pimeloyl-diphenyl ether)	200—220°C.	1.93

The Viscosity Ratios were measured at 25°C on a 1% solution in ortho-chlorophenol. Concentrated solutions in ortho-chlorophenol were converted into films by evaporation and into fibres by spinning into acetone or methanol.

#### EXAMPLE 6

##### *Poly(glutaryldiphenyl ether)*

- 10 Poly(glutaryldiphenyl ether) was prepared as described in Example 1, but using glutaryl chloride (4.23 parts) instead of sebacoyl chloride. The polymer had a Viscosity Ratio, measured at 25°C on a 1% solution in dichloroacetic acid, of 1.75. A concentrated solution in dichloroacetic acid was spun into water to give fibres. The polymer showed no sign of flowing up to 340°C, and underwent decomposition before this temperature.

#### EXAMPLE 7

- 20 Example 1 was repeated but using carbon bisulphide instead of methylene chloride as the solvent. The product had a Viscosity Ratio of 1.27, measured at 25°C on a 1% solution in ortho - chlorophenol.

#### EXAMPLE 8

- 25 Example 1 was repeated but using sym - tetrachloroethane instead of methylene chloride as the solvent, and omitting the period under reflux. The product had a Viscosity Ratio of 1.51, measured at 25°C on a 1% solution in ortho - chlorophenol.

#### EXAMPLE 9

- 35 Example 1 was repeated but replacing a proportion of the diphenyl ether with biphenyl. The co-polymers containing diphenyl ether and biphenyl in molar ratios 90:10, 80:20, and 75:25 had Viscosity Ratios (1% in ortho - chlorophenol at 25°C) of 2.02, 1.88, and 1.19. All three were soluble in ortho - chlorophenol and dichloro - acetic acid, and the first two gave strong, coherent films and fibres; the third had too low a molecular weight to give strong films and fibres. Co - polymers containing 30 moles % or more of biphenyl were insoluble in ortho - chlorophenol and dichloroacetic acid.

#### EXAMPLE 10

##### *Poly(carbonyl diphenyl ether)*

- To dry methylene chloride (25 parts) was added aluminium chloride (4.675 parts). The mixture was cooled to -70°C, then a solution of para - phenoxy - benzoyl chloride (5.9 parts) in dry methylene chloride (25 parts) was added with stirring. The mixture was allowed to warm to room temperature then to stand at room temperature for 48 hours. The mixture was poured into dilute hydrochloric acid, methylene chloride was boiled off, and the solid product was isolated, extracted with acetone, and dried. The polymer was reprecipitated from dichloroacetic acid by methanol, washed well with methanol, and dried. The polymer, whose structure is believed to be mainly poly(4:4' - carbonyl-diphenyl ether), had a Viscosity Ratio (1% in dichloroacetic acid at 25°C) of 1.57, showed no sign of flowing up to 350°C, had a glass-rubber transition temperature of 185°C, and was wet spun from a concentrated solution in dichloroacetic acid into methanol to give strong coherent fibres.

#### EXAMPLE 11

##### *Poly(isophthaloyldiphenyl ether)*

- Diphenyl ether (4.25 parts) was dissolved in dry methylene chloride (50 parts). The solution was cooled, with stirring, to -70°C and aluminium chloride (9.35 parts) was added followed by isophthaloyl chloride (5.1 parts). The mixture was allowed to warm up gradually to room temperature; after 1 hour the temperature was about -20°C, and soon thereafter perceptible darkening of the solution occurred. The mixture was stirred for 6 hours, allowed to stand overnight, then refluxed for 30 minutes, cooled and poured into dilute hydrochloric acid. The methylene chloride was boiled off and the residual solid was filtered off, dried at 125°C, ground up, boiled with dilute hydrochloric acid, and again filtered off and dried. The poly(isophthaloyl diphenyl ether) so obtained was crystalline, and melted at 275—285°C. It was soluble in ortho - chlorophenol, metacresol, dichloroacetic acid and concentrated sulphuric acid, and had a Viscosity Ratio (measured on a 1% solution

by weight in ortho - chlorophenol at 25°C) of 1.60. A saturated solution in ortho - chlorophenol at room temperature contained about 10 parts by weight of the polymer in 100 volumes, and was spun from a hypodermic syringe into a bath of acetone or methanol to give filaments which were readily handleable, and which were drawn in contact with a hot surface at 180°C to give strong fibres. Evaporation of the solution gave a tough film. A film was also prepared by pressing the poly(isophthaloyl - diphenyl ether) at 270°C with a pressure of 15 tons per square inch. The resulting film was coherent, very flexible and extremely tough.

#### EXAMPLE 12

##### *Poly(terephthaloyldiphenyl ether)*

Aluminium chloride (9.35 parts) was added to dry methylene chloride (50 parts) at -70°C, followed by diphenyl ether (4.25 parts). Terephthaloyl chloride (5.1 parts) was added with stirring, and the mixture was allowed to rise slowly to room temperature. After a total time of 5 hours, the mixture was refluxed for 30 minutes, cooled, and poured into dilute hydrochloric acid. The methylene chloride was boiled off, the residual slurry was boiled for one hour, and the solid was collected and dried at 120°C. The resulting poly(terephthaloyl - diphenyl ether) was birefringent and underwent no apparent change on heating to 350°C.

#### EXAMPLE 13

##### *Poly(methoxyterephthaloyldiphenyl ether)*

Diphenyl ether (2 parts) was dissolved in dry methylene chloride (15 parts) and the solution was cooled to -70°C. Aluminium chloride (4.4 parts) was added with stirring, followed by methoxyterephthaloyl chloride (2.6 parts). The mixture was stirred for 6 hours, during which time its temperature rose gradually to room temperature, allowed to stand overnight, then added to dilute hydrochloric acid. Methylene chloride was boiled off and the residual slurry was boiled, cooled, and filtered. The product, poly(methoxy - terephthaloyldiphenyl ether), was crystalline and melted at 300—320°C.

#### EXAMPLE 14

Poly(isophthaloyldiphenyl ether) was prepared as described in Example 11. The polymer had a Viscosity Ratio, measured at 25°C. on a 1% solution in ortho - chlorophenol, of 1.73, and an intrinsic viscosity  $[\eta]$

where 
$$[\eta] = \lim_{c \rightarrow 0} \frac{[\eta]_{\text{nsp}}}{c}$$
 of 0.64

#### EXAMPLE 15

Poly(benzophenone - 4:4' - dicarbonyldiphenyl ether) and poly(diphenylmethane -

4:4' - dicarbonyldiphenyl ether) were prepared using the method described in Example 11 but using equivalent amounts of the appropriate acid chlorides instead of isophthaloyl chloride. The polymers melted respectively at 370—380°C. and 254—256°C.

#### EXAMPLE 16

A co - polymer was prepared as described in Example 11 but replacing half of the isophthaloyl chloride by terephthaloyl chloride. This co - polymer, a 50:50 random co - polymer of poly(isophthaloyl diphenyl ether) and poly(terephthaloyldiphenyl ether), had a Viscosity Ratio (1% in ortho - chlorophenol at 25°C.) of 123, and did not melt at temperatures up to 320°C. It could be wet spun from orthochlorophenol into methanol to give weak, brittle fibres.

#### EXAMPLE 17

##### *Poly(sebacoylbiphenyl)*

To methylene chloride (67 parts) was added aluminium chloride (9.35 parts). The mixture was cooled to -70°C, then biphenyl (3.85 parts) was added with stirring, followed by sebacoyl chloride (7.0 parts) dissolved in methylene chloride (13.4 parts). The mixture was allowed to warm up slowly to room temperature, refluxed for half an hour and then poured into cold dilute hydrochloric acid. The methylene chloride was boiled off and the polymer filtered off, washed well with dilute hydrochloric acid and water, and dried at 120°C. The infra-red spectrum showed that the polymer was essentially a polyketone, containing little or no free chlorocarbonyl, anhydride, or carboxyl groups.

#### EXAMPLE 18

##### *Poly(carbonylbiphenyl)*

To methylene chloride (13.4 parts) was added aluminium chloride (6.05 parts). The mixture was cooled to -70°C, then biphenyl - 4 - carbonyl chloride (3 parts) dissolved in methylene chloride (33.5 parts) was added with stirring at -70°C. The mixture was allowed to warm to room temperature over about one hour, kept at room temperature overnight, refluxed for half an hour, then poured into cold dilute hydrochloric acid. Polymer remaining in the flask was also treated with cold dilute hydrochloric acid. The methylene chloride was boiled off, and the polymer was filtered off, washed with dilute hydrochloric acid and water, and dried. The product was poly(carbonylbiphenyl), which did not melt up to 310°C.

#### EXAMPLE 19

##### *Poly(sebacoyldiphenylmethane)*

Example 17 was repeated but using diphenylmethane (4.2 parts) instead of biphenyl. The polymer did not soften at temperatures up to 320°C.

## EXAMPLE 20

*Poly(terephthaloyldiphenylmethane)*

Example 19 was repeated but using terephthaloyl chloride (6.1 parts) instead of sebacoyl chloride. The polymer did not soften at temperatures up to 320°C.

## EXAMPLE 21

*Poly(sebacoylbibenzyl)*

Example 17 was repeated but using bibenzyl (4.6 parts) instead of biphenyl. The polymer melted at 183°C.

## EXAMPLE 22

*Poly(sebacoyl - 1:3 - diphenylpropane)*

Example 17 was repeated but using 1:3 diphenylpropane (4.9 parts) instead of biphenyl. After the reactants reached room temperature they were stirred for 2 hours at room temperature then worked up by addition to dilute hydrochloric acid as described in Example 17. The product melted at 165—170°C.

## EXAMPLE 23

*Poly(sebacoyl - 1:2 - diphenoxyethane)*

A mixture of aluminium chloride (9.35 parts) and dry methylene chloride (33.5 parts) was cooled to -70°C with stirring, then a solution of 1:2 diphenoxyethane (5.35 parts) and sebacoyl chloride (6.0 parts) in dry methylene chloride (33.5 parts) was added. The temperature was brought back to -70°C then allowed to rise to room temperature. The mixture was poured into dilute hydrochloric acid, the methylene chloride was boiled off, and the product was filtered off, washed with dilute hydrochloric acid and water, and dried. The polymer had a Viscosity Ratio, measured as a 1% solution in orthochlorophenol at 25°C, of 1.32, and a crystalline melting point of 210—223°C.

## EXAMPLE 24

*Poly(sebacoyl - 1:4 - diphenoxybutane)*

This polymer, prepared as in Example 23, but using 1:4 - diphenoxybutane (6.0 parts) instead of 1:2 diphenoxyethane, had a crystalline melting point of 201—212°C.

## EXAMPLE 25

*Poly(sebacoyldibenzofuran)*

A mixture of methylene chloride (67 parts), aluminium chloride (9.35 parts), and dibenzofuran (4.2 parts) was cooled to -60°C, then sebacoyl chloride (6.0 parts) was added with stirring and the mixture was cooled to -70°C and allowed to warm up to room temperature over 4 hours. The mixture was added to cold dilute hydrochloric acid, the methylene chloride was boiled off, and the product was isolated, washed, and dried. The polymer softened at 80—105°C.

## EXAMPLE 26

*Poly(sebacoylfluorene)*

Example 25 was repeated using fluorene (4.15 parts) instead of dibenzofuran. The

polymer did not soften at temperatures up to 300°C.

## EXAMPLE 27

*Poly(sebacoyldiphenyl sulphide)*

Example 25 was repeated using diphenyl sulphide (4.65 parts) instead of dibenzofuran. The polymer melted at 173—173°C.

## EXAMPLE 28

*Poly(sebacoylstilbene)*

Example 25 was repeated using stilbene (4.5 parts) instead of dibenzofuran. The polymer did not melt at temperatures up to 300°C.

## EXAMPLE 29

*Poly(sebacoyldibenzyl ether)*

To a stirred mixture of aluminium chloride (9.35 parts) in dry methylene chloride (26.8 parts) at -70°C was added sebacoyl chloride (6.0 parts), followed after 5 minutes by a solution of dibenzyl ether (5.0 parts) in methylene chloride (40.2 parts). The reaction mixture was allowed to warm up over 3 hours to room temperature then poured into cold dilute hydrochloric acid. The product was filtered off, washed with water, and dried.

## EXAMPLE 30

Example 23 was repeated using 2:2' - dimethyldiphenyl ether (5.0 parts) instead of 1:2 diphenoxyethane. The polymer was an amorphous solid which softened at 118—122°C to a viscous liquid, and had a Viscosity Ratio as a 1% solution in orthochlorophenol at 25°C of 1.36.

## EXAMPLE 31

1:10 - Diphenyldecane (2.9 parts), sebacoyl chloride (2.4 parts) and aluminium chloride (3.5 parts) were added to dry carbon bisulphide (30 parts). The mixture was refluxed gently for 2 hours, allowed to stand for 48 hours, then poured into cold dilute hydrochloric acid. The aqueous slurry was heated on a steam-bath for 2 hours, and the insoluble material collected and extracted with hot water and ethanol. The product, poly(sebacoyl - 1:10 - diphenyldecane), had a Viscosity Ratio, measured at 25°C on a 1% solution in orthochlorophenol, of 1.37 and a birefringent melting point of 150—155°C. It was readily melt-spun at 235°C to give drawable filaments.

## EXAMPLE 32

Diphenyl ether (4.25 parts) and aluminium chloride (9.35 parts) were dissolved in dry methylene chloride (20 parts) and cooled to -60°C, then a solution of diphenyl ether 3:3' - dicarbonyl chloride (7.375 parts) in dry methylene chloride (30 parts) was added slowly with stirring at -60°C. The reaction mixture was allowed to warm up to room temperature, left overnight, then added to dilute hydrochloric acid. Methylene chloride was boiled off, and the product was isolated and washed well with water. The polymer, poly(diphenyl

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70

75

80

85

90

95

100

105

110

115

120

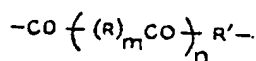
ether 3:3' - dicarbonyldiphenyl ether), had a Viscosity Ratio (1% in ortho - chlorophenol at 25°C) of 1.78.

### EXAMPLE 33

- 5 Dry methylene chloride (200 parts) was cooled to -80°C and aluminium chloride (6.6 parts), 1:2 - diphenoxyethane (4.28 parts), and a solution of isophthaloyl chloride (4.06 parts) in dry methylene chloride (50 parts) were successively added with stirring. After 10 2 hours at -70°C the mixture was allowed to warm to room temperature and kept at room temperature overnight. The mixture was added to dilute hydrochloric acid and methylene chloride was boiled off on a steam bath. 15 The product was isolated, dried, and reprecipitated from ortho - chlorophenol with methanol. The product, poly(isophthaloyl - 1:2 - di - phenoxy ethane), had a birefringent melting point at 220-225°C and could be melt-spun to fibres.

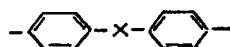
### WHAT WE CLAIM IS:—

1. A fibre and film forming polyketone, as hereinbefore defined, containing the repeating unit:

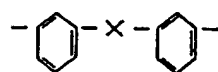


where R is a radical chosen from the group consisting of

- (i) a divalent aliphatic radical,  
 (ii) a divalent radical chosen from the group consisting of



and

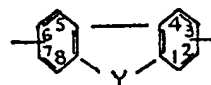


- where X is chosen from the group consisting of



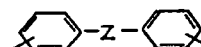
- and each aromatic nucleus may be unsubstituted, as shown, or may contain from one to four substituents, each of which may be chosen from the group consisting of  $\text{CH}_3$ —,  $\text{CH}_3\text{O}$ —,  $\text{C}_2\text{H}_5\text{O}$ —,  $\text{C}_3\text{H}_7\text{O}$ —,  $\text{F}$ —,  $\text{Cl}$ — and  $\text{Br}$ —, (iii) a divalent aromatic radical which may be mono or bi nuclear and may be a condensed ring nucleus and the nucleus in each case may be unsubstituted or may be substituted in the manner described in (ii), (iv) a mixed alkyl/aryl diradical, the aromatic nucleus of which may be unsubstituted or may be substituted in the manner described in (ii),  $\text{R}'$  is a radical chosen from the group consisting of

(a)



where Y is —O—, —CH<sub>2</sub>— or —S—, which may be unsubstituted, as shown, or may be substituted in either or both aromatic nuclei by from one to three substituents, each of which may be chosen from the group consisting of alkyl, alkoxy, F—, Cl— and Br—,

(b)



Z is —A—, —O—A—O—, —S—, —CH=CH—, —CH<sub>2</sub>—O—CH<sub>2</sub>—, —O— or a direct linkage

A is alkylene,

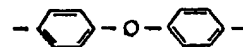
and either or both of the aromatic nuclei may be unsubstituted or may be substituted with one to four substituents, each of which may be chosen from the group consisting of alkyl, alkoxy, F—, Cl—, and Br—.

m is zero or one

n is zero or one

2. A fibre and film forming polyketone according to Claim 1, wherein R is a divalent aliphatic radical, and m, n = 1.

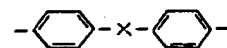
3. A fibre and film forming polyketone according to Claim 1, wherein R' is



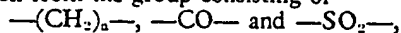
4. A fibre and film forming polyketone according to Claim 3, wherein R is a divalent aliphatic radical and m and n are each equal to one.

5. A fibre and film forming polyketone according to Claim 3, wherein R is a divalent aromatic radical and m and n are each equal to one.

6. A fibre and film forming polyketone according to Claim 3, wherein R is:

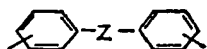


X is a covalent bond or a divalent radical chosen from the group consisting of



$n$  is an integer from 1 to 10 and m and n are each equal to one.

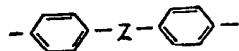
7. A fibre and film forming polyketone according to Claim 1, wherein R' is



Z is  $-A-$ ,  $-O-A-O-$ ,  $-S-$ ,  
 $-CH=CH-$ ,  $-CH_2-O-CH_2-$ ,  $-O-$   
 or a direct linkage

5 A is an alkylene diradical.

8. A fibre and film forming polyketone  
 according to Claim 1, wherein  $R^1$  is

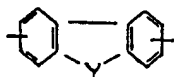


10 where Z is  $-A-$ ,  $-O-A-O-$ ,  $-S-$ ,  
 $-CH=CH-$ ,  $-CH_2-O-CH_2-$ ,  $-O-$  or  
 a direct linkage.

A is an alkylene diradical.

9. A fibre and film forming polyketone  
 according to Claim 1, wherein  $R^1$  is

15



where Y is  $-O-$ ,  $-CH_2-$  or  $-S-$

10. A fibre and film forming polyketone  
 according to Claim 5, wherein the aromatic  
 diradical is 1:4 phenylene.

20 11. A fibre and film forming polyketone

according to Claim 5, wherein the aromatic  
 diradical is 1:3 phenylene.

12. A fibre and film forming polyketone  
 according to Claim 6, wherein X is  
 $-(CH_2)_n-$

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13. A fibre and film forming polyketone  
 according to Claims 2—13, wherein the aromatic  
 nuclei are substituted according to  
 Claim 1.

14. A fibre and film forming polyketone  
 according to Claim 13, wherein the nuclei are  
 substituted by methoxy.

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15. A process for the preparation of a poly-  
 ketone according to any of the preceding  
 Claims by the reaction of the compound  
 $H-R^1-H$ , wherein  $R^1$  is as hereinbefore  
 defined, with an acid chloride.

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16. A process according to Claim 15, where-  
 in the reaction is carried out in the presence  
 of a diluent.

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17. A process according to Claim 15 or 16,  
 wherein the reaction is carried out in the  
 presence of a Friedel Crafts catalyst.

18. A fibre and film forming polyketone as  
 hereinbefore described, with particular refer-  
 ence to the Examples.

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19. A process for the preparation of a poly-  
 ketone as hereinbefore described, with particu-  
 lar reference to the Examples.

20. Fibres and films prepared from the poly-  
 ketones claimed in Claims 1—14 inclusive and  
 in Claim 18.

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Agent for the Applicants,  
 WALTER SCOTT.